REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*

2. REPORT DATE
30 August 1997

3. REPORT TYPE AND DATES COVERED
Technical

4. TITLE AND SUBTITLE

SYNTHESIS AND CHARACTERIZATION OF TERT-BUTYLGALLIUM-ANTIMONY COMPOUNDS: X-RAY CRYSTAL STRUCTURES OF t-$Bu_3Ga \bullet Sb(SiMe_3)_3$, $[t$-$Bu_2GaSb(SiMe_3)_2]_2$, AND t-$Bu_2GaSb(SiMe_3)_2Ga(t$-$Bu)_2Cl$, THE FIRST EXAMPLE OF A GALLIUM-ANTIMONY MIXED-BRIDGE COMPOUND

5. FUNDING NUMBERS

N00014-95-1-0194
R&T Project 3135008---16

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8. PERFORMING ORGANIZATION REPORT NUMBER

Technical Report
No. DU/DC/TR-71

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Office of Naval Research
300 North Quincy Street
Arlington, VA 22217-5000

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

Accepted for publication in *Organometallics*

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for Public Release
Distribution Unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

The 1:1 mole ratio reaction of t-Bu_3Ga with $Sb(SiMe_3)_3$ in hexane yields the expected Lewis acid-base adduct t-$Bu_3Ga \bullet Sb(SiMe_3)_3$ (**1**). The 1:1 mole ratio dehalosilylation reaction of t-Bu_2GaCl with $Sb(SiMe_3)_3$ yields the dimeric compound $[t$-$Bu_2GaSb(SiMe_3)_2]_2$ (**2**). The mixed-bridge compound t-$Bu_2\overline{GaSb(SiMe_3)_2Ga(t\text{-}Bu)_2Cl}$ (**3**) was isolated from both the 2:1 reaction of t-Bu_2GaCl with $Sb(SiMe_3)_3$ and the 2:1 equilibration of t-Bu_2GaCl with **2**. These new gallium-antimony compounds have been characterized through multinuclear solution NMR spectroscopy, partial elemental analysis, and single-crystal X-ray structural analysis. In addition, compound **2** was found to produce nanocrystalline GaSb with an approximate average particle size of 9 nm upon thermolysis at 400 °C under vacuum.

14. SUBJECT TERMS

gallium-antimony compounds, synthesis, structure
snaocrystalline gallium antimonide

15. NUMBER OF PAGES
22

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT
Unclassified

18. SECURITY CLASSIFICATION OF THIS PAGE
Unclassified

19. SECURITY CLASSIFICATION OF ABSTRACT
Unclassified

20. LIMITATION OF ABSTRACT
Unlimited

OFFICE OF NAVAL RESEARCH

Grant N00014-95-1-0194
R&T Project 3135008---16

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Technical Report No. DU/DC/TR-71

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Accepted for Publication in *ORGANOMETALLICS*

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30 August 1997

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(Received ....; Accepted ....)

REVISED/ ACCEPTED/ VERSION

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Abstract- The 1:1 mole ratio reaction of t-Bu_3Ga with $Sb(SiMe_3)_3$ in hexane yields the expected Lewis acid-base adduct t-$Bu_3Ga{\bullet}Sb(SiMe_3)_3$ (**1**). The 1:1 mole ratio dehalosilylation reaction of t-Bu_2GaCl with $Sb(SiMe_3)_3$ yields the dimeric compound $[t\text{-}Bu_2GaSb(SiMe_3)_2]_2$ (**2**). The mixed-bridge compound $t\text{-}Bu_2\overline{GaSb(SiMe_3)_2Ga(t\text{-}Bu)_2Cl}$ (**3**) was isolated from both the 2:1 reaction of t-Bu_2GaCl with $Sb(SiMe_3)_3$ and the 2:1 equilibration of t-Bu_2GaCl with **2**. These new gallium-antimony compounds have been characterized through multinuclear solution NMR spectroscopy, partial elemental analysis, and single-crystal X-ray structural analysis. In addition, compound **2** was found to produce nanocrystalline GaSb with an approximate average particle size of 9 nm upon thermolysis at 400 °C under vacuum.

Introduction

The bulk of our recent research into potential precursor compounds to 13-15 materials has focused primarily on Group 13 metals and the pnicogens phosphorus and arsenic[1]. These compounds have been isolated largely in the form of 1:1 Lewis acid-base adducts[2] and dimeric compounds containing an $\overline{M\text{-}E\text{-}M\text{-}E}$ type core[1b,3]. These dimeric compounds are generally obtained through either dehalosilylation or lithium halide elimination reactions, by combining R_2MX (R = alkyl, aryl; X = Cl, Br) in a 1:1 ratio with $E(SiMe_3)_3$ or $LiE(SiMe_3)_2$ (E = P, As), respectively. Less common are compounds containing a mixed-bridge type core ring of the form $\overline{M\text{-}E\text{-}M\text{-}X}$ (X = Cl[3d,4] or Br[4b]), obtained from dehalosilylation of R_2MX and $E(SiMe_3)_3$ in a 2:1 ratio, or equilibration of a dimeric compound with two equivalents of R_2MX.

In an attempt to extend our methodologies to the formation of precursors to Group 13-antimonides, we have recently reported the synthesis and characterization of the adducts $Et_3Ga{\bullet}Sb(SiMe_3)_3$ and $(Me_3SiCH_2)_3In{\bullet}Sb(SiMe_3)_3$, as well as the oligomeric compounds $[(Me_3CCH_2)_2GaSb(SiMe_3)_2]_x$ and $[(Me_3SiCH_2)_2InSb(SiMe_3)_2]_2$[5]. We, as well as others, have also demonstrated that nanocrystalline GaSb is obtained from the 1:1 dehalosilylation reaction of $GaCl_3$ and $Sb(SiMe_3)_3$ in pentane solution[6]. These results show that further study into this area is indeed warranted, as does the lack of known Group 13-antimony compounds[7-10]. In an effort to further expand the library of known Group 13-antimony compounds, herein we report the synthesis and complete characterization of t-$Bu_3Ga{\bullet}Sb(SiMe_3)_3$ (**1**), $[t$-$Bu_2GaSb(SiMe_3)_2]_2$ (**2**), and t-$Bu_2GaSb(SiMe_3)_2Ga(t$-$Bu)_2Cl$ (**3**), the first gallium-antimony mixed-bridge compound. In addition, the thermal decomposition of **2** was examined in order to assess the suitability of these compounds as precursors to GaSb.

Experimental Section

General Considerations: All manipulations of air- and moisture-sensitive materials were performed in a Vacuum Atmospheres HE-493 Dri-Lab containing an argon atmosphere or by standard Schlenk techniques. Hexane and toluene were distilled over sodium/potassium alloy under dry dinitrogen. t-Bu_3Ga[11], t-Bu_2GaCl[11], and $Sb(SiMe_3)_3$[12] were prepared from literature procedures. $GaCl_3$ was purchased from Strem Chemicals and used as received. The integrity of all starting materials was confirmed using ^1H NMR spectroscopy. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian Unity XL-400 spectrometer operating at 400 and 100.6 Mhz, respectively. ^1H and $^{13}C\{^1H\}$ spectra were

referenced to TMS using the residual protons or carbons of deuterated benzene at δ 7.15 or δ 128.0, respectively. All NMR samples were prepared in 5-mm tubes which were septum-sealed under argon. Melting points (uncorrected) were obtained with a Thomas-Hoover Uni-melt apparatus, using capillaries that were flame-sealed under argon. Elemental analyses (EA) were performed by E+R Microanalytical Laboratory, Inc., Corona, NY. Powder X-ray diffraction (XRD) data were collected on a Phillips XRG-3000 diffractometer utilizing Cu-Kα radiation. IR spectra of volatile gases were acquired using a gas cell on a BOMEM Michelson MB-100 FT-IR spectrometer. TGA/DTA analyses were obtained on a TA Instruments SDT 2960 simultaneous TGA/DTA apparatus.

Preparation of t-Bu_3Ga•$Sb(SiMe_3)_3$ (1): t-Bu_3Ga (0.241 g, 1.00 mmol) in 20 mL of hexane was added to a 250 mL Schlenk flask equipped with a stir bar and Teflon valve. $Sb(SiMe_3)_3$ (0.341 g, 1.00 mmol) in 20 mL of pentane was added slowly via pipet and the clear, slightly red solution was stirred overnight at room temperature. The solvent was reduced *in vacuo* to yield a red liquid, which was cooled to -30 °C to produce brown prismatic crystals of **1**, suitable for X-ray analysis (0.533 g, 92% yield). m.p. 103 - 107 °C. Anal. Calcd. (found) for $C_{21}H_{54}GaSbSi_3$: C, 43.31 (43.13); H, 9.35 (9.27). ^{1}H NMR: δ 0.41 (s, 27H, -$SiMe_3$), δ 1.28 (s, 27H, -CH_3). ^{13}C NMR{^{1}H}: δ 4.86 (s, -$SiMe_3$), δ 32.11 (s, -CH_3).

Preparation of [t-$Bu_2GaSb(SiMe_3)_2$]$_2$ (2): t-Bu_2GaCl (0.242 g, 1.10 mmol) dissolved in 25 mL of hexane was added to a 250 mL Schlenk flask equipped with a stir-bar and Teflon valve. $Sb(SiMe_3)_3$ (0.375 g, 1.10 mmol) dissolved in 25 mL of hexane was

added to the flask dropwise via pipet, resulting in a clear, light yellow solution which was stirred for 1 d at room temperature. After this period, the solution had taken on a dark yellow color. The solution volume was reduced *in vacuo,* and then stored at -30 °C for several days. Colorless crystals of **2**, suitable for X-ray analysis were isolated (0.342 g, 45% yield). m.p. 220 °C (dec. to a red liquid). Anal. Calc. (found) for $C_{28}H_{72}Ga_2Sb_2Si_4$: C, 37.20 (37.10); H, 8.03 (7.95). ^{1}H NMR: δ 0.37 (s, 36H, -SiMe$_3$), δ 1.21 (s, 36H, CH$_3$-). ^{13}C{^{1}H} NMR: δ 4.79 (s, -SiMe$_3$), δ 30.77 (s, -CH$_3$).

Preparation of *t*-Bu$_2$GaSb(SiMe$_3$)$_2$Ga(*t*-Bu)$_2$Cl (3):

(Method 1): [*t*-Bu$_2$GaSb(SiMe$_3$)$_2$]$_2$ (0.174 g, 0.20 mmol) partially dissolved in 20 mL of hexane was added to a 250 mL Schlenk flask equipped with a stir-bar and Teflon valve. A small amount of toluene (approximately 5 mL) was added to increase the solubility. t-Bu$_2$GaCl (0.084 g, 0.4 mmol) in 20 mL of toluene was added via pipet, resulting in a clear amber solution which was allowed to stir at room temperature for 2.5 d. The solvent was reduced *in vacuo* yielding a red liquid which was allowed to evaporate at -30 °C for 3 d, producing colorless, prismatic crystals of **3**, suitable for X-ray analysis (.097 g, 36% yield). m.p. 174 - 182 °C (dec. to a red liquid). Anal. Calc. (found) for $C_{22}H_{54}Ga_2SbSi_2Cl$: C, 39.35 (39.12); H, 8.11 (7.98). ^{1}H NMR: δ 0.49 (s, 18H, -SiMe$_3$), δ 1.32 (s, 36H, CH$_3$-). ^{13}C{^{1}H} NMR: δ 6.05 (s, -SiMe$_3$), δ 30.82 (s, -CH$_3$).

(Method 2): *t*-Bu$_2$GaCl (0.316 g, 1.44 mmol) dissolved in 25 mL of hexane was added to a 250 mL Schlenk flask. Sb(SiMe$_3$)$_3$ (0.245 g, 0.72 mmol) dissolved in 25 mL of hexane was added to the flask dropwise via pipet, resulting in a clear, light yellow solution which was stirred for 5 d at room temperature. After 1 d, the solution began to take on a

golden color, and gradually continued to darken. The solution volume was reduced *in vacuo*, and then evaporated at -30 °C. Colorless crystals of **3** formed, as confirmed by ^1H NMR analysis (0.099 g, 21% yield).

Thermal Decomposition of 2. (a) TGA Analysis: Figure 4 shows the weight loss of **2** under nitrogen flow with a 5 °C/min heating rate. Segment 1: 150 - 200 °C with 44 % weight loss. Segment 2: 250 - 400 °C with 5 % weight loss. Total observed weight loss: 52 %. Total calculated weight loss for GaSb formation: 57.6 %

(b) Pyrolysis at 400 °C: The sample (0.227 g, 0.50 mmol based on the monomeric unit) was loaded into a sublimator and heated under dynamic vacuum as follows: 175 °C, 15 min; 200 °C, 10 min; 400 °C, 12 h. A black residue was present on the cold finger, and a metallic mirror had formed on the base of the sublimator wall during this time. A gray/black powder was recovered (0.061g, 64 % yield based on GaSb), and its identity confirmed through comparison of the d-spacings and line intensities obtained by XRD analysis with those of GaSb (JCPDS file 7-215). The approximate average particle size of 9 nm was calculated using the Scherrer equation. Anal. Calc. (found) for GaSb: Ga, 36.41 (35.17); Sb, 63.59 (61.96). The Ga:Sb ratio was 1.00:1.01. A second sample of **2** (0.198 g, 0.44 mmol based on the monomeric unit) was decomposed as described above, with the exception that static vacuum was used and a -196 °C cold trap was attached in an attempt to study the volatiles formed during decomposition. The results were as follows: noncondensable CH_4 and H_2, approximately 0.5 mmol total (0.3 mmol CH_4 and 0.2 mmol H_2); condensable $HSiMe_3$ and iso-butylene, approximately 0.53 mmol total. CH_4, $HSiMe_3$, and iso-butylene were identified by IR spectroscopy. The

0.023 g of black powder recovered (27 % yield based on GaSb) was identified through XRD and analyzed for impurities. Anal. Calc. (found) for this second sample: C, 0.0 (2.28); H, 0.0 (0.99).

X-ray structural solution and refinement

Crystal, data collection, and refinement parameters are given in Table 1, while selected bond lengths and angles are presented in Figures 1, 2, and 3. ORTEP diagrams showing the solid state conformations of **1** - **3** can be found in Figures 1 through 3, respectively. Compound **1**: A suitable crystal was selected and mounted in a nitrogen-flushed glass capillary. The unit-cell parameters were obtained by the least-squares refinement of the angular settings of 24 reflections ($20° \leq 2\Theta \leq 25°$). The systematic absences in the diffraction data are consistent for the space groups $Pna2_1$ or $Pnma$. The E-statistics and the presence of a molecular mirror plane in the molecule suggested the centrosymmetric option which was subsequently verified by chemically reasonable and computationally stable results of refinement. The structure was solved using direct methods, completed by subsequent difference Fourier syntheses and refined by full-matrix least-squares procedures. Absorption corrections were not necessary because there was less than 10% variation in the integrated ψ-scan intensities. The molecule is located on a mirror plane. All non-hydrogen atoms were refined with anisotropic displacement coefficients and hydrogen atoms were treated as idealized contributions. All software and sources of the scattering factors are contained in the SHELXTL (Version 5.3) program library (G. Sheldrick, Siemens XRD, Madison, WI).

Compounds **2** and **3**: Single crystals of **2** and **3** were mounted on a glass fiber with

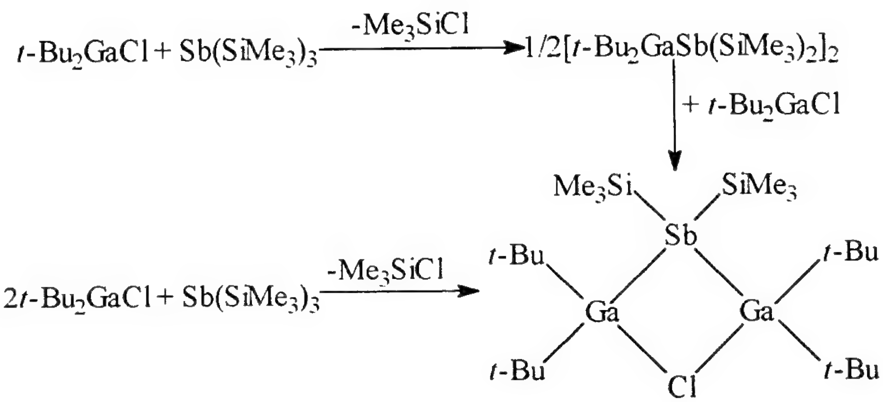
a viscous oil under a stream of cold dinitrogen. X-ray intensity data were recorded at -135 °C on a Siemens SMART CCD diffractometer utilizing graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) and the structures were solved by direct methods. Full-matrix least-squares refinement with weights based upon counting-statistics was performed. Hydrogen atoms were incorporated at their calculated positions using a riding model in the later iterations of refinement which converged at R = 0.032 (R_w = 0.041) for **2** and R = 0.050 (R_w = 0.053) for **3**. A final difference Fourier synthesis revealed no unusual features. Crystallographic calculations were performed using the NRCVAX[13] suite of structure determination programs. For all structure-factor calculations, neutral atom scattering factors and their anomalous dispersion corrections were taken from ref. 14.

Results and Discussion

The 1:1 mole ratio reaction of t-Bu_3Ga and $Sb(SiMe_3)_3$ affords in high yield the expected Lewis acid-base adduct t-$Bu_3Ga{\bullet}Sb(SiMe_3)_3$ (**1**). The 1:1 mole ratio dehalosilylation reaction of t-Bu_2GaCl with $Sb(SiMe_3)_3$ yielded the dimeric compound [t-$Bu_2GaSb(SiMe_3)_2]_2$ (**2**), while the 2:1 mole ratio reaction of t-Bu_2GaCl with $Sb(SiMe_3)_3$ resulted in the formation of t-$Bu_2\overline{GaSb(SiMe_3)_2Ga(t\text{-}Bu)_2Cl}$ (**3**) after 5 days. Initially, the reaction was stopped after 1 day, and the only products isolated were **2** and t-Bu_2GaCl. Interestingly, the attempted formation of $\overline{Ga\text{-}E\text{-}Ga\text{-}Cl}$ core structures through 2:1 reactions yields a wide variety of results. The 2:1 reaction of $(Me_3CCH_2)_2GaCl$ with $P(SiMe_3)_3$ fails to yield the mixed-bridge, instead forming $[(Me_3CCH_2)(Cl)GaP(SiMe_3)_2]_2$[3d]. In the case of $(Me_3CCH_2)_2GaCl$ reacted 2:1 with

$As(SiMe_3)_3$, the expected mixed-bridge was formed after 5 days[4c], comparable to the time involved in the formation of **3**. Also noteworthy is the reaction of t-Bu_2GaCl with $As(SiMe_3)_3$, which failed to undergo dehalosilylation in 1:1 or 2:1 ratios, and the mixed-bridge was obtained only from reaction of $[t\text{-}Bu_2GaAs(SiMe_3)_2]_2$ with t-Bu_2GaCl[15]. The mixed-bridge **3** was also obtained from the equilibration reaction of t-Bu_2GaCl with **2** in a 2:1 mole ratio. These reactions are summarized in Scheme 1. Compound **3** is interesting due to the possibility of metathetical reactions involving the ring chlorine atom and a $LiE(SiMe_3)_2$ (E = P, As) salt to form the rare mixed-pnictogen structure. This possibility is currently under investigation. The solid-state structures of **1**, **2**, and **3** have been confirmed through single crystal X-ray analysis.

Scheme 1



Compound **1** crystallizes in the orthorhombic space group *Pnma*. The Ga-Sb bond length of 3.027(2) Å in this structure is significantly longer than the bond length of 2.846(5) Å reported for the adduct $Et_3Ga{\bullet}Sb(SiMe_3)_3$[5]. This discrepancy can be explained by the extreme steric bulk of the t-butyl- group in comparison to the ethyl- group, which prevents close approach of the $Sb(SiMe_3)_3$ moiety. It should also be noted

that the ligands bound to the metal centers adopt a staggered conformation in relation to one another.

Crystals of the dimeric compound **2** belong to the monoclinic space group *C2/c* and lie on a two-fold axis. The average Ga-Sb bond length of 2.7666(7) Å found in **2** is slightly longer than the average Ga-Sb bond length of 2.66 Å reported for the ring compound $[Cl_2GaSb(t\text{-}Bu)_2]_3$[7]. Again, this is probably due to the steric bulk exerted by the *t*-butyl- groups. The average endocyclic bond angles in **2** are 94.45(3)° for Ga-Sb-Ga and 85.549(24)° for Sb-Ga-Sb. The gallium and antimony atoms in this compound reside in distorted tetrahedral environments and the core ring is planar.

The mixed-bridge compound **3** forms crystals belonging to the triclinic space group $P\bar{1}$. The average Ga-Sb bond length of 2.7336(11) Å compares well with the analogous bond length in **2** (*vide supra*). The core ring of this compound is again planar, with average endocyclic Ga-Sb-Ga, Ga-Cl-Ga, and Sb-Ga-Cl ring angles of 85.68(3)°, 98.18(9)°, and 88.07(6)°, respectively. The gallium and antimony atoms again reside in distorted tetrahedral environments, with the influence of the *t*-butyl- groups demonstrated in the appropriate bond angles.

In an attempt to assess the utility of these compounds as precursors to GaSb, the thermal decomposition behavior of **2** was closely examined. This compound was found to produce reasonably pure GaSb in moderate to low yield. In addition, analysis of the volatile products produced during decomposition suggests that the formation of GaSb occurs through a β-hydride elimination pathway. This is evidenced through the condensation of $HSiMe_3$ and iso-butylene in the cold trap, the expected products of such

an elimination process. Both compounds were identified by IR spectroscopy. If this elimination occurred cleanly, the theoretical amount of $HSiMe_3$ and iso-butylene collected would be 1.76 mmol total (based on 0.44 mmol of starting material). The fact that approximately a third of this amount, 0.53 mmol, was observed suggests that the elimination was not complete, and a secondary process was also involved. Two other noncondensable gasses were produced during the pyrolysis, namely CH_4 and H_2, presumably from decomposition of the -$SiMe_3$ groups. It is possible to envision a two step mechanism for **2** undergoing β-hydride elimination and subsequently forming GaSb, with elimination of iso-butylene as step 1 followed by elimination of trimethylsilane as step 2. However, the TGA plot for this process, shown in Figure 4, indicates only one major elimination occurring, in the range of 150 - 200 °C. This suggests that steps 1 and 2 occur simultaneously. The small (approximately 10 %), broad weight loss observed from 250 - 400 °C is probably due to evolution of residual silicon and carbon containing species not lost in the initial elimination, and could account for the observed CH_4 and H_2 gas. It should be noted that initial pyrolysis experiments on **1** indicate that GaSb is also formed, however the purity and yield are less than observed for **2**, and the system is still under investigation.

Acknowledgment - We wish to thank the Office of Naval Research for their financial support of this work.

Supplementary Material Available: Tables of bond distances, bond angles, anisotropic temperature factor parameters, and fractional coordinates for **1**, **2**, and **3** (26 pages). Ordering information is given on any current masthead page.

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Captions to Figures

Figure 1. Molecular structure of **1** drawn with 30% probability ellipsoids. Methyl- group carbon atoms are rendered spherically due to their high thermal activity. Bond Lengths (Å): Ga-Sb: 3.027(2); Sb-Si(1): 2.555(2); Ga-C(6): 2.007(8); Sb-Si(2): 2.566(3); Ga-C(10): 2.027(9). Bond Angles (°): Ga-Sb-Si(1): 118.53(6); Sb-Ga-C(6): 98.7(3); Ga-Sb-Si(2): 114.68(7); Sb-Ga-C(10): 102.8(3); Si(1)-Sb-Si(2): 100.65(8); C(6)-Ga-C(10): 116.7(3); Si(1)-Sb-Si(1)A: 100.75(13); C(6)-Ga-C(6)A: 117.5(5).

Figure 2. ORTEP diagram (30% probability ellipsoids) showing the solid-state structure and atom numbering scheme for **2**. Hydrogen atoms are omitted for clarity. Bond Lengths (Å): Ga1-Sb1: 2.7684(7); Ga1-Sb2: 2.7648(7); Ga1-C31: 2.018(6); Sb1-Si1: 2.5918(17); Ga1-C41: 2.036(5); Sb2-Si2: 2.5827(18). Bond Angles (°): Ga1-Sb1-Ga1: 94.37(3); Ga1-Sb2-Ga1: 94.53(3); Sb1-Ga1-Sb2: 85.549(24); C31-Ga1-Sb1: 115.30(18); C41-Ga1-Sb1: 109.61(16); C31-Ga1-Sb2: 110.54(17); C41-Ga1-Sb2: 112.76(18); Si1-Sb1-Ga1: 115.83(4); Si2-Sb2-Ga1: 118.74(4); C31-Ga1-C41: 118.5(3); Si1-Sb1-Si1: 96.52(6); Si2-Sb2-Si2: 96.13(6); Si1A-Sb1-Ga1: 117.98(4); Si2A-Sb2-Ga1: 115.22(5).

Figure 3. ORTEP diagram (30% probability ellipsoids) showing the solid-state structure and atom numbering scheme for **3**. Hydrogen atoms are omitted for clarity. Bond Lengths (Å, average): Ga1-Sb1: 2.7336(12); Ga2-Sb1: 2.7337(11); Ga1-Cl1: 2.4568(24); Ga2-Cl1: 2.462(3); Ga1-C11: 2.032(9); Ga1-C21: 2.007(9); Ga2-C31: 2.019(8); Ga2-C41: 2.007(9); Sb1-Si1: 2.599(3); Sb1-Si2: 2.599(3). Bond Angles (°, average): Ga1-Sb1-Ga2: 85.68(3); Ga1-Cl1-Ga2: 98.18(9); Sb1-Ga1-Cl1: 88.12(6); Sb1-Ga2-Cl1: 88.01(6); C11-Ga1-Sb1: 117.4(3); C11-Ga1-Cl1: 105.7(3); C21-Ga1-Sb1: 111.8(3); C21-Ga1-Cl1: 103.9(3); C11-Ga1-C21: 122.5(4); C31-Ga2-C41: 122.4(4); C31-Ga2-Sb1: 117.4(3); C31-Ga2-Cl1: 105.5(3); C41-Ga2-Sb1: 112.09(25); C41-Ga2-Cl1: 103.6(3); Si1-Sb1-Ga1: 120.81(7); Si1-Sb1-Ga2: 117.42(6); Si2-Sb1-Ga1: 117.34(7); Si2-Sb1-Ga2: 120.85(7); Si1-Sb1-Si2: 96.93(8).

Figure 4. Thermogravimetric Analysis (TGA) data for the decomposition of [*t*-$Bu_2GaSb(SiMe_3)_2]_2$ (**2**).

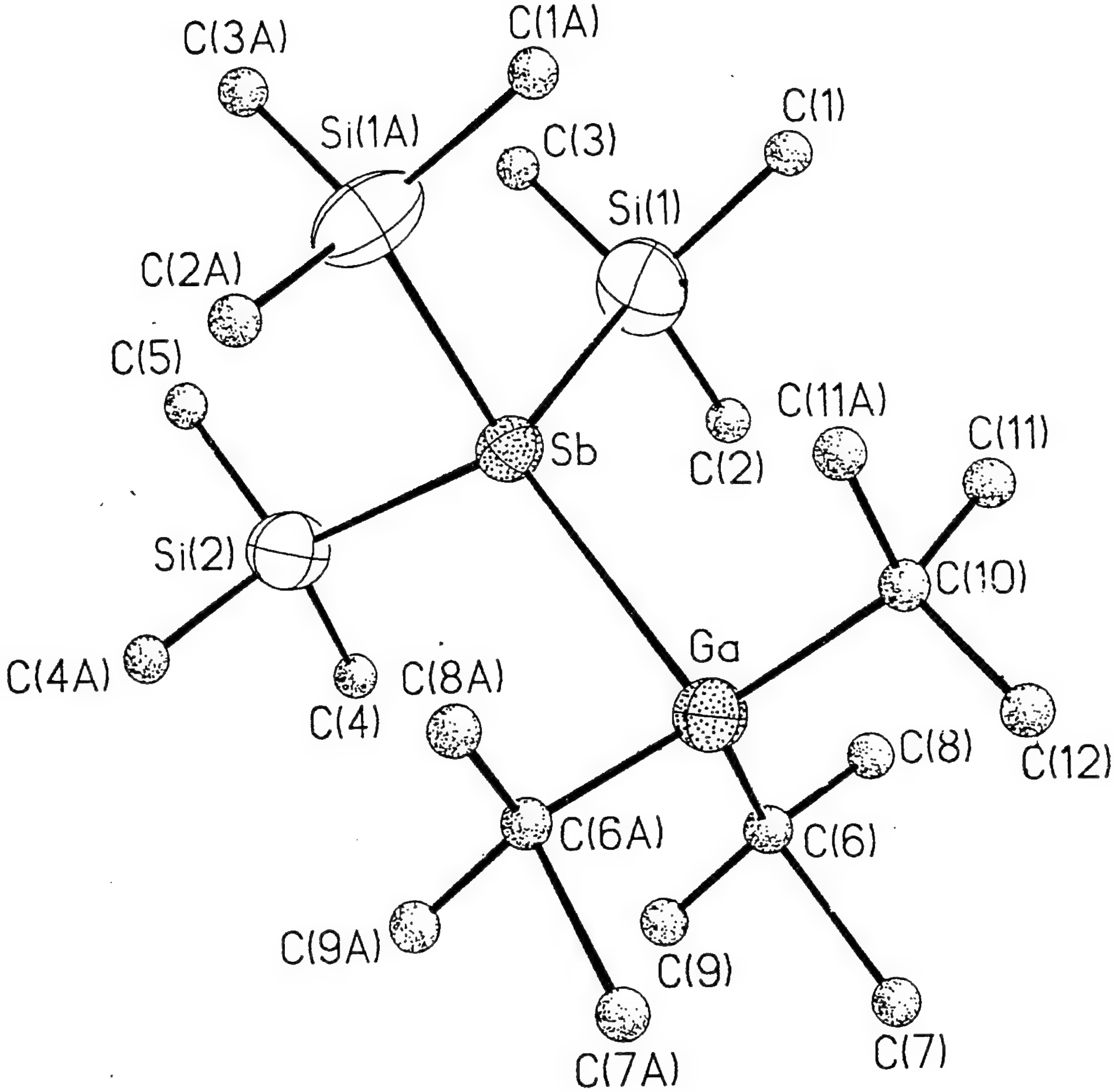
C(3A)
C(1A)
Si(1A)
C(3)
C(1)
Si(1)
C(2A)
C(5)
Sb
C(2)
C(11A)
C(11)
Si(2)
C(10)
C(4A)
Ga
C(4)
C(8A)
C(8)
C(12)
C(6A)
C(6)
C(9A)
C(9)
C(7A)
C(7)

Figure 1.

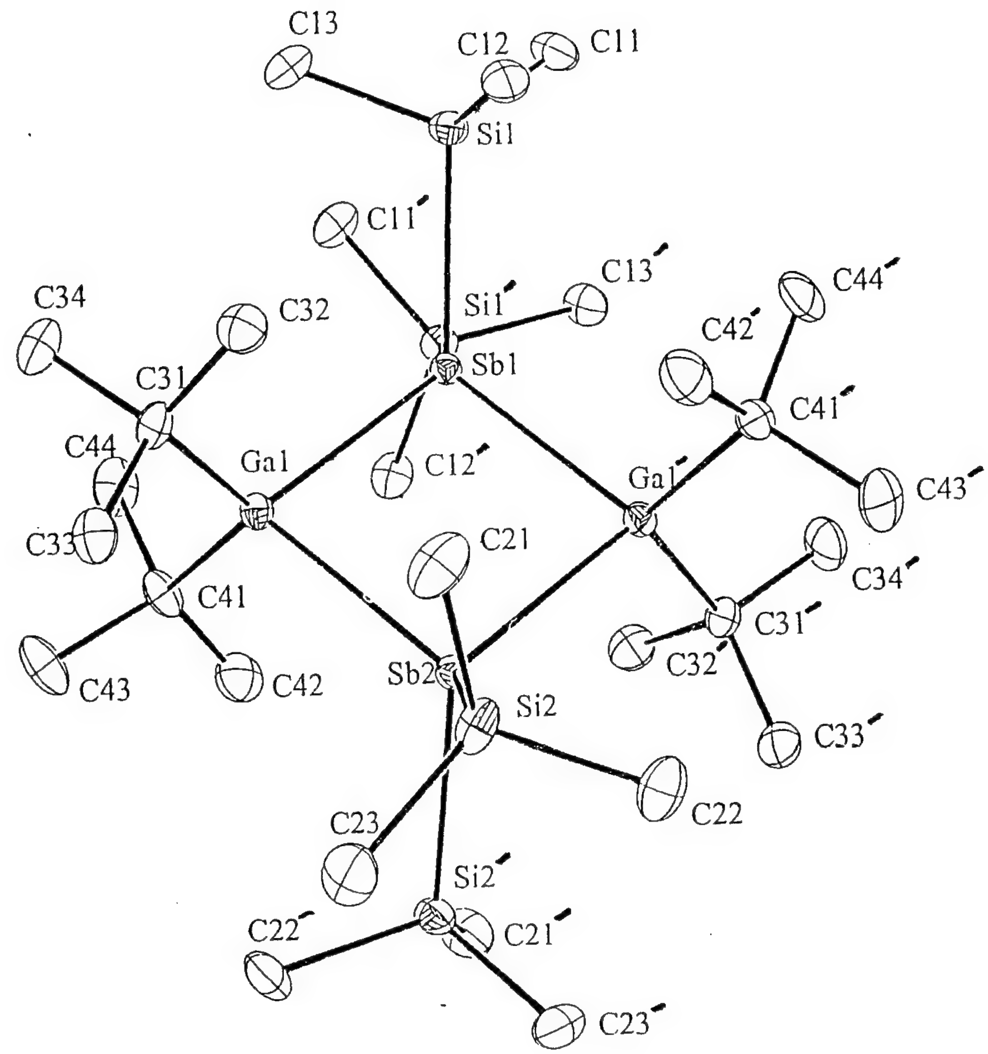
C13
C12
C11
Si1
C11'
Si1'
C13'
C34
C32
C44'
C42'
Sb1
C31
C41'
C44
Ga1
C12'
Ga1'
C43'
C33
C21
C34'
C41
C31'
C43
C42
Sb2
Si2
C32'
C33'
C22
C23
Si2'
C22'
C21'
C23'

Figure 2.

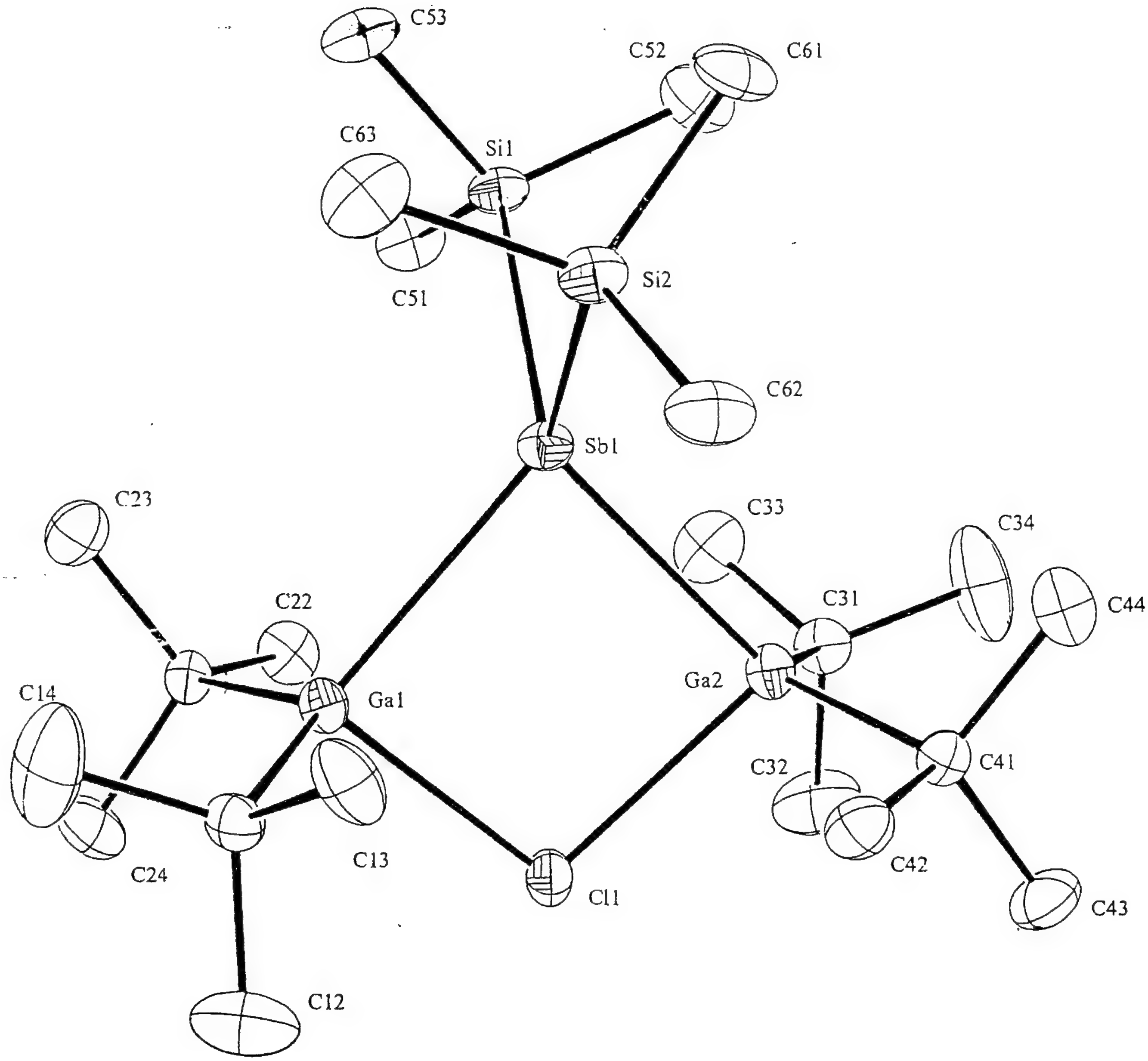
C53
C52
C61
C63
Si1
Si2
C51
C62
Sb1
C23
C33
C34
C22
C31
C44
C14
Ga1
Ga2
C32
C41
C24
C13
C42
Cl1
C43
C12

Figure 3.

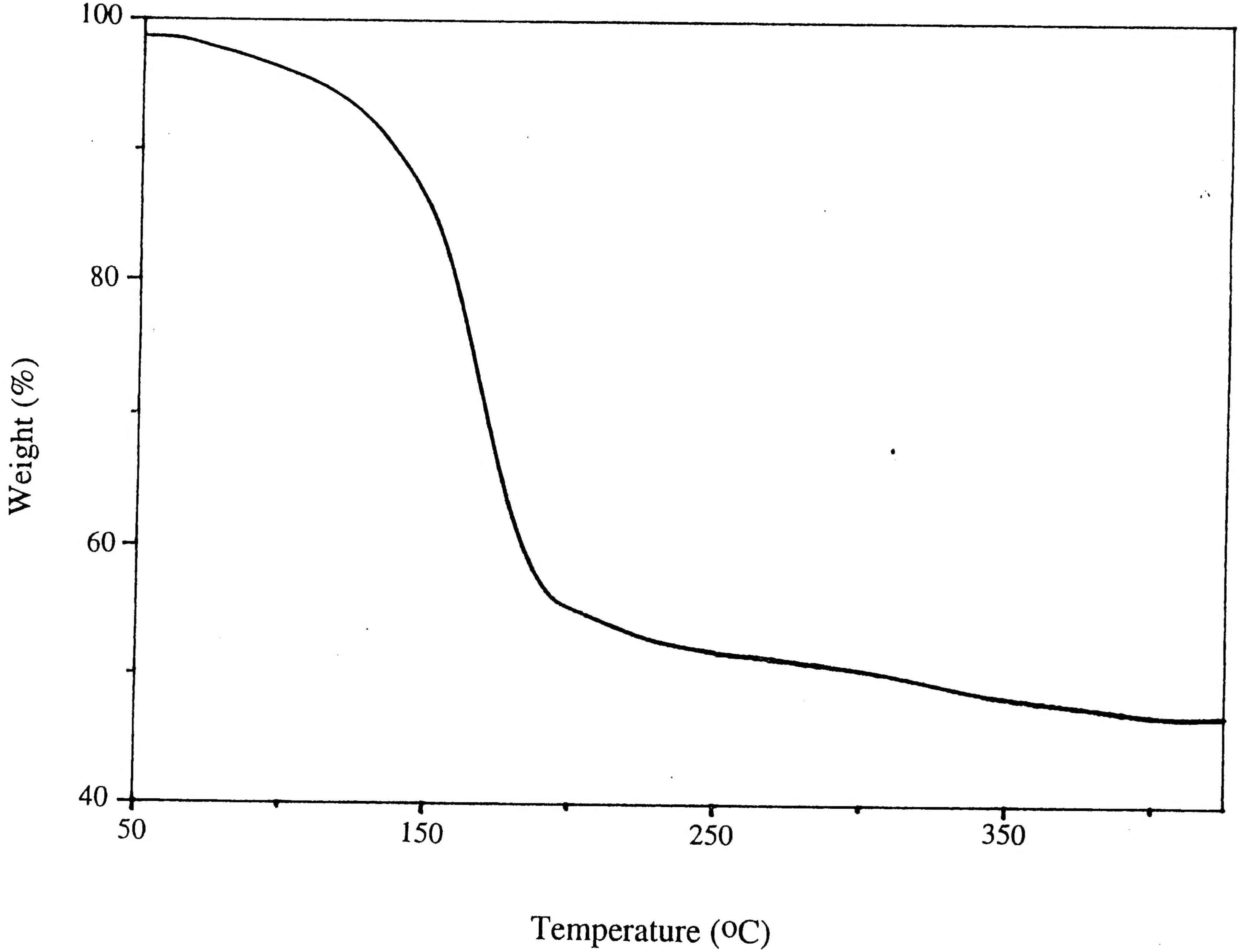

Figure 4.

Table 1. Crystallographic Data for t-$Bu_3Ga \bullet Sb(SiMe_3)_3$ (**1**), [t-$Bu_2GaSb(SiMe_3)_2]_2$ (**2**), and t-$Bu_2\overline{GaSb(SiMe_3)_2Ga(t\text{-}Bu)_2Cl}$ (**3**).

	1	**2**	**3**
formula	$C_{21}H_{54}GaSbSi_3$	$C_{28}H_{72}Ga_2Sb_2Si_4$	$C_{22}H_{54}Ga_2SbSi_2Cl$
formula weight	582.38	904.15	671.47
space group	*Pnma*	*C2/c*	$P\bar{1}$
a, Å	17.504(3)	19.614(4)	10.0358(4)
b, Å	15.923(3)	13.280(3)	11.5969(5)
c, Å	11.522(5)	18.230(3)	16.3753(7)
α, deg.	---	---	82.2250(1)
β, deg.	---	116.912(12)	72.1790(1)
γ, deg.	---	---	64.3690(1)
V, Å^3	3209(2)	4234.2(14)	1635.83(12)
Z	4	4	2
crystal color, habit	brown block	colorless block	colorless block
D(calc), g cm^{-3}	1.206	1.418	1.363
μ(MoKα), cm^{-1}	17.98	26.5	26.2
temp, K	245(2)	138	138
radiation		MoKα (λ = 0.71073 A)	
R(*F*), %	4.31[a]	3.2[b]	5.0[b]

Table 1. (cont.)

$R(wF^2)$, %	10.16[a]	4.1[b]	5.3[b]

[a] Quantity minimized = $R(wF^2) = \Sigma[w(F_o^2-F_c^2)^2]/\Sigma[(wF_o^2)^2]^{1/2}$; $R = \Sigma\Delta/\Sigma(F_o)$, $\Delta = |(F_o-F_c)|$

[b] Quantity minimized = $\Sigma[w(F_o-F_c)^2]/\Sigma[(wF_o)^2]^{1/2}$; $R = \Sigma\Delta/\Sigma(F_o)$, $\Delta = |(F_o-F_c)|$

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